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(54) Process for the enzymatic hydrolysis of fish proteins and resulting products.

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(18)

This invention covers the obtaining of certain products of high biological value which have nutritional, therapeutic or cosmetological dietetic use, and that are well-accepted by both human beings and animals. More precisely, it covers proteolyzates (that is, protein hydrolyzates) prepared by enzymatic means from whole and newly-caught fish, in other words, from natural protein-rich substances, which proteins will never be denatured during the treatments according to the process. The invention also covers said process with its variations, making use of a characteristic association of equipment, which can, in whole or in part, be installed on fishing vessels.

Fishing products and by-products are protein-rich raw materials with high nutritional value. Various processes have been utilized in order to extract these proteins or the polypeptides and amino acids derived from them. Thus, it has been possible to obtain fish protein concentrates, fish flours, fish solubles. These products are neither hydrolyzates nor autolysates and are not within the scope of this invention. They are all the result of preparation processes that denature the protein substance.

For a long time, people have sought to prepare proteolyzates that would contribute the small peptides necessary for a normal diet balanced in terms of specific amino acids, or for dietetic, therapeutic or cosmetological use, capable, in other words, of correcting certain deficiencies in one or more amino acids.

To do this, there have been proposals, based on natural proteins, involving on the one hand chemical hydrolysis catalyzed by acids or bases, and, on the other, enzymatic hydrolysis.

Chemical hydrolysis presents the known advantages which are those of chemical operations over microbiological operations, in other words, a smaller useful volume, easier control of the various parameters of the reaction, stability of

the reagents, etc. On the other hand, it entails amino acid losses that vary in terms of the nature of the acids themselves; the hydrolyzate no longer has the natural balanced composition of the initial protein, which represents a major drawback. Moreover, it is accompanied by isomerization of the L-amino acids (natural series) into D-amino acids, generally without biological value. Finally, acid or alkaline hydrolysis also involves other non-protein components of the raw material and releases among other things fatty acids or soaps; these untreated hydrolyzates therefore readily produce emulsions that are often problematic.

Enzymatic hydrolysis is generally carried out by enzymes, hereinafter called exogenous enzymes, added to the natural protein dispersion to be hydrolyzed. For example, these include: pepsins, trypsins, papain, bromelin, ficin, fungal or bacterial proteases, etc. The initial enzymes to be natural protein material will be referred to below as endogenous. True autolyses, in other words, hydrolyses obtained with endogenous enzymes alone, result in hydrolyzates of very debatable quality. Bacterial and (or) fungal hydrolyses, either uncontrolled (because of bacterial contamination) or channeled (because of deliberate seeding with certain microbial strains) are superimposed on this autolysis and at times even become dominant. Depending on the currently known enzymatic hydrolysis processes, one (or more) chemical activators) is/are used along with exogenous enzymes. The hydrolysis is carried out at a high temperature that is highly prejudicial to the conservation of the protein material in its natural state. In certain cases, the proteins are even denatured ahead of time by heating. Moreover, acids, bases and salts are added to fix the pH and ionic force and to increase the solubility of the protein and of the products of hydrolysis. If the operation is carried out at extreme pH levels (for example, close to 2 in the pepsin hydrolyses or close to 9 for certain trypsin hydrolyses), one again runs into the problems of chemical hydrolysis which is then superimposed on the true enzyme hydrolysis. The addition of chemical activators, in addition to the exogenous enzymes used, introduces an additional biological factor into the final product, which is not desirable. This is the case, for example, with papain, ficin and bromelin, which

are activated in classic fashion by cyanides, sulfurated hydrogen, cystein, glutathione and other reducing compounds.

In certain cases, exogenous enzymes are produced on site by the culture of suitable microbes in the presence of the initial protein. This hydrolysis by controlled microbial cultures (with pure strains) presents all the difficulties inherent in the process, which is very difficult to implement. At the same time, it introduces a number of foreign ingredients into the final product: products from microbial metabolism, products of the degradation of the raw material by hydrolyses or fermentation other than proteolyses alone, microbial proteins, etc. The same is true, a fortiori, in hydrolyzates obtained by uncontrolled microbial cultures; it is true of the autolyzates already cited. Moreover, in the latter, bacteriological purity is not obtained and is difficult to control. This results in unstable or unacceptable organoleptic features.

In all these processes, the biological value does not correspond to the value of the initial protein. This is why it has not been possible to date to exploit rationally the value of the treatment by hydrolysis (and even more so by other processes) starting with fresh fish on the sites where they are caught or in the immediate proximity of these areas. In point of fact, there was no process that made it possible to benefit fully from the natural value of the protein substance contained in the freshly caught fish. In addition, all these processes ultimately lead to products from which it is very difficult to extract lipids by means of mechanical processes. In effect, the classic hydrolyzates very readily form stable emulsions that are difficult to break down by centrifuging. The lipid levels of the final product are then relatively high. This results in a certain instability of the organoleptic characteristics during storage. The extraction of lipids by specific solvents is also often difficult and ever more costly. In any case, it is not recommended because it would then be necessary to eliminate the last traces of solvent and prevent any reactions between these solvents and the biological constituents of the proteolyzate.

The characteristic enzymatic hydrolysis, the proteolyzates thus obtained and the corresponding production facility covered by the invention, make it possible to prevent the above-cite drawbacks. Among other things, they include the following industrial results:

- The protein raw material of animal origin is treated in its natural stage without any

denaturing either by heat or by the prior action of salts or solvents or other denaturing reagents. The product thus obtained is truly representative of the initial protein. The fully ground-up fish has been initially manipulated only once, for purposes of sorting, as it emerges from the trawl, for example, moving directly then into the treatment group.

The enzymatic type hydrolysis results from the joint and highly accelerated action of the endogenous proteolytic enzymes (which are proper and specific to the raw material) and exogenous proteolytic enzymes (added in the form of enzyme preparations or extracts), exclusive of any parallel action. Proteolysis is faster than that done by the same ferments acting separately. It does not involve the action of any exogenous chemical activators. As indicated above, it simultaneously respects the natural balanced composition of the protein to be hydrolyzed and the natural configuration of the amino acids present, or in other words, their biological value.

The fact that one starts with a substance (fish) that is practically living, generally makes it possible to better separate the different fractions after hydrolysis according to the invention. The invention covers only the protein constituents of the raw material, which limits the formation of emulsions during the fractionation and purification operations; in particular, the lipids can be extracted more easily and more effectively by centrifuging. The organoleptic features (smell, color, taste) and

the stability of the proteolyzates are thereby substantially improved. The flavor of the hydrolyzate is that of a biologically intact fresh product. Moreover, it is easy to neutralize these organoleptic characteristics and to prevent their reappearance; it is possible to improve control of microbial purity; all these results are obtained thanks to treatment of the untreated hydrolyzates by one or more substances such as peroxides.

The technology of the process is simple and flexible, which makes it possible to obtain at will hydrolyzates with characteristics adapted to the different forms of exploitation and utilization envisaged. This simplicity also makes it possible to install all or part of the equipment on board fishing vessels, thus ensuring the freshness of the material to be hydrolyzed. It should be noted that "junk" fish (or unmarketable fish, generally rejected at sea) are fully and perfectly recoverable by the process according to the invention.

In sum, the process and the production facility according to the invention make it possible to obtain high quality proteolyzates. The latter are themselves characterized by a high biological value, representative of the initial protein and of the stable organoleptic qualities particularly favorable to their acceptability in food, dietetics, therapy and cosmetology. Their color is very light, the smell is nearly no-existent or very slight, and there is little or no taste. The consistency can range from the liquid state to the pasty or solid state (dry powder). Their solubility in water can be nearly totally, only partial or almost nil, at will. This feature is obtained by varying the relative volumes of two of the fractions (one soluble and the other not very soluble) of the hydrolyzate after separation. This variation is a function of the degree of hydrolysis selected in terms of the process. A major result, which is new as compared to the characteristics of known products, therefore is represented by total or practically non-existent solubility (at will) of the product, and by adjustment of the degree of this solubility.

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This invention may be better understood from the following text, which includes:

- A short summary of the principal characteristics of the process;
- A description and detailed explanation of the process, phrase by phrase,
- The citation as non-limiting examples of analysis results of hydrolyzates that can be obtained from certain fishery products,
- The description of a form of embodiment of the necessary installation, also cited as a non-limiting example.

The explanation of the process and of the installation are accompanied by the following diagrams:

Figure 1 a diagram of the necessary phases and stages, with the different possibilities and variations, to obtain the desired alimentary products. The reference letters are defined in the text explaining the process.

Figure 2 a schematic front view of the on-board installation according to one form of embodiment, said installation including operations through the pasteurization phase.

Figure 3 a horizontal projection of said on-board installation.

Figure 4 a horizontal projection of the shore installation (operation following flash-pasteurization).

The process is characterized mainly in that the hydrolysis operation involves a very fresh substrate, ground into a fine paste as soon as possible in or near the place where the fish are caught. This hydrolysis is carried out under temperature and pH as well as ionic force conditions such that the protein material is never denatured and the endogenous enzymes are not altered. Activation of the hydrolysis

is carried out on the said conditions by addition of particular exogenous enzymes, which exogenous enzymes are the object of a reinforcing synergic, in other words accelerant, action of the endogenous enzymes. This joint action makes it possible to reduce the hydrolysis time substantially without denaturing the protein substance. The fact that the starting substrate is fresh, then treated as indicated above, permits an easy separation operation of the three fractions of the hydrolyzate (specifically, the lipids). The same factor makes it possible to obtain fractions with little smell and color, in which the deodorizing, decolorizing and antiseptic action of certain peroxides in dilute solution will be more effective and easier. Other characteristics of the process will be clear from the following detailed explanation.

The process begins with a substrate consisting of fresh fish (phase P of the diagram in Figure 1), in other words, fish in a state such that the proteolytic enzymes of the fish are still active or activatable. In practice, this means that the fish must be processed, if possible, as soon as it is caught and, in any event, before it has gone beyond the rigor mortis stage. The protein to be hydrolyzed is therefore not degraded, and the endogenous proteolytic enzymes are intact.

a) The entire fish is then subjected to suitable grinding into a fine paste (phase A of Figure 1).

b) The hydrolysis is then done in one or more tanks, in an agitated medium protected against microbial contamination (operation B, per Figure 1). In some cases, the presence of fresh or salt water can facilitate the hydrolysis. In no event should the saline concentration lead to the denaturing of the proteins. Hydrolysis is obtained through the joint action of the natural proteolytic enzymes (or endogenous enzymes), and of one or more suitable exogenous enzymes incorporated by addition to the tank. The term suitable exogenous enzymes means enzymes whose action is potentialized (in other words, stimulated or accelerated) by the presence of one or more natural fish enzymes. This is the case, for example, with pronase



(*Streptomyces griseus* protease, which is activated by a muscular cathepsin of the fish (active at a pH between 6.3 and 6.5), and by a visceral enzyme whose maximum activity is at a pH of between 7.5 and 8.

The simultaneous and joint action of the endogenous enzymes and of the exogenous enzyme or enzymes is much faster than the separate action of each of them in the same temperature, pH, ionic force and concentration conditions. The time gained per degree of given progress of the hydrolysis can exceed 50% with respect to the hydrolysis time with the exogenous enzymes only. This potentialization is most favorable under the physical and chemical maximum activity conditions of the exogenous ferment (pH, temperature, concentration) but can also take place very suitably outside these optimum zones, provided the substrate is fresh. Thus, in the above example, it is preferable to cause the pronase to act at pH 6 to 6.5 on very fresh fish, rather than at its optimum activity pH (7.4 to 8) on fish that is not as fresh or that has been denatured by heating, which deactivates the cathepsins and other endogenous enzymes.

The duration of the hydrolysis depends on the quantity of soluble products desired, as explained in the course of the description of the terminal phases. In principle, to get good results, the hydrolysis lasts around one and a half hour. It is done at a temperature that is always less than the temperature at which the endogenous proteolytic enzymes begin to become inactive, and to the temperature at which the protein substance begins to be denatured. It has been found, for example, that the optimum temperature is approximately 56° centigrade. The untreated hydrolyzate thus obtained can then be treated in different ways as shown in the diagram in Figure 1 (C, D or E below, explained in paragraphs c, d, e). Operations C and D are merely variants.

c) Once hydrolysis occurs, the enzymes may be inactivated permanently by heating (operation G). In that case, it is sufficient to heat the mass to a temperature

and for a period of time determined by experience, generally 90 to 100° for 5 to 20 minutes. At this stage, experience shows that once the proteins are hydrolyzed, there is no further fear of denaturing by heating.

d) It is also possible to inactivate the enzymes reversibly through the addition of a suitable inhibitor, for example an oxidant such as a peroxide or other substance determined in terms of the type of exogenous enzyme used. This constitutes operation D. This addition, which is known, in this particular case constitutes a variant that may be of interest. It can be used for exploitation reasons, when, for example, it is desirable to stop the hydrolysis at an intermediate stage, to store (or transport) the product in its condition and then restart the hydrolysis elsewhere, at a later time, up to a more advanced stage. The necessary quantity of inhibitors will then be added and mixed thoroughly in the mass, in order to inactivate the enzymes, for example, a quantity of hydrogen peroxide corresponding to a concentration of 0.5% by volume of oxygen, calculated with respect to the total mass of hydrolyzate. At the proper time, this inhibitor will be destroyed by conventional means. The hydrogen peroxide also has the advantage of protecting the medium against microbial contamination.

e) To separate the hydrolyzate from non-hydrolyzable wastes (miscellaneous debris, bones, scales, etc.), the product is passed through a suitable screen. This operation E (Figure 1) is generally carried out after the hydrolysis operation B, without any need for enzyme inactivation operations C and D. These waste products can be recovered.

f) If applicable, this is followed by a flash-pasteurization phase (Operation F).

g) When the hydrolyzates have been prestabilized by an inhibitor according to phase D, the process can be accompanied at this point by treatment (Operation G) with a very dilute peroxide solution (in principle less than 1%), or any other similar

substance. This treatment can be done cold or hot by simple addition for a few minutes. The excess peroxide or similar substance is destroyed in the subsequent phases, during reheating for subsequent centrifuging or during spray drying.

This treatment simultaneously decolorizes, sterilizes and deodorizes the product without causing the appearance of amino oxides. This is understandable because the hydrolysis, if carried out as indicated, furnishes only peptides and amino acids without any appearance of amines through the decarboxylation of the latter. Experience has demonstrated the excellent stability of the fresh products in storage. This treatment may be postponed to subsequent phases, such as J2 and J3 described below.

h) After phase E, or phase F or phase G, the product obtained may be stored, if necessary, in spaces (for example, the holds of ships) at 0° centigrade. This is phase H.

i) This product is then pumped and possibly transported to a place (phase I) where it undergoes the following operation.

j) Phase J consists of reheating and centrifuging to separate the lipids from the proteolyzate. This can come either after phase E or phase F or phase G, or the following phases H and I (depending on whether the product was stored earlier, or not). It has been found that following hydrolysis done in this manner, such separation is substantially easier and can be done mechanically, for example in a centrifuge, at an appropriate temperature. In general, it is preferable to work hot, for example, at between 50 and 70° Centigrade. These temperatures depend on the characteristics of the centrifuges used. This separation is done after the addition of water, which is done either at the beginning of this phase J, or at the hydrolyzate stage (phase B) or during these two phases (B and J), provided the total quantity of water represents approximately half the weight of fresh fish. Going back to the

separation by centrifuging, three fractions are therefore recovered (see diagram, Figure 1):

- A light and clear lipid fraction (J1), which has a better appearance, with less smell, and is preserved better than the raw oil extracted directly and classically from the same raw material.
- A more or less thick pasty fraction (J2),
- An aqueous solution (J3) of intermediate density.

The latter two fractions consist of peptides and amino acids. The ones that correspond to the water solution are soluble; those in the pasty fraction are less soluble, or insoluble. However, these fractions have substantially the same relative proportions of the various amino acids, in other words, whether they have the same balanced amino acid composition as the initial protein, but distributed into peptides of different molecular weights. The relative size of these two fractions depends on the degree of hydrolysis that has been attained; this degree can therefore be adjusted in terms of the solubility desired for the proteolyzate. A short hydrolysis will result in few soluble products. Conversely, if the hydrolysis is continued almost to its theoretical finish, the result will be almost entirely a water-soluble hydrolyzate.

After the first separation, the pasty fraction can be washed in water or with a dilute saline solution in order to extract by a second separation the soluble parts that will then join the aqueous solution known as the soluble hydrolyzate.

Peroxide (or a similar substance) can be added if desired to each of the two fractions J2 and J3, postponing at that point operation G described above.

k) The lipid fraction (J1) can be refined directly by a treatment K. This treatment includes, for example, a mechanical separation and a steam treatment. It makes it possible to obtain a clear odorless oil without peroxide.

l) The other two fractions (J2 and J3) (pasty fraction and aqueous solution) can then be treated together or separately, depending on whether a partly or fully soluble product is desired.

In all cases, the treatment can consist of a concentration Q, using a known process (such as evaporation in a vacuum), followed by drying S, done by spraying or freeze-drying, for example.

In the event fractions J2 and J3 are treated together (operation L), the product can be extracted after operation Q (viscous state) or after operations Q and S (dry powder), or after drying S only (dry powder).

m) The pasty fraction J2 can be treated (operation M) separately. It is either concentrated at Q (viscous or semi-liquid products), or dried directly by a medium S, or concentrated and dried. In these latter two cases, a slightly colored, but very poorly soluble, is obtained.

n) The fraction in a water solution (J3) can be treated (operation N), also separately by concentration in a vacuum Q, followed by drying S. Using mechanical processes, this produces a white, soluble powder with a lipid content on the order of 1%. The importance of this fraction (J3) with respect to the pasty fraction (J2) is a function of the duration of the hydrolyzate. The solubility of a product in accordance with operation L (J2 and J3) is therefore also a function of the state of advancement attained by the hydrolysis B.

The heating of the aqueous and pasty fractions in terms of the concentration in a vacuum and of the drying eliminates the any excess peroxide introduced in G, and ensures the disappearance of any trace of enzymatic action, if necessary.

The products are preferably presented in the form of dry powders with a high protein content (content expressed as a percentage of total nitrogen x 6.25). The powder from the pasty fraction J2 is beige in color, with a very faint smell and taste. The powder from the water solution J3 is white: it has no smell, no taste, and is entirely soluble.

This general explanation of the process and of the resulting products is completed by the results of the non-limiting example given below.

#### Example of treatment:

The substrate consisted of 1000 kg of blue whiting (or Poutassou or *Micromesistius Poutassou* whiting) and black Pollock (or hake or *Pollachius Virens*). The ground fish was introduced into a tank with an agitator, after adding 500 kg of water. Ficin (exogenous enzymes) was added in the proportion of 0.8 per mil in relation to the weight of the fish, or 0.800 kg. The product was maintained at 55° Centigrade for 90 minutes.

After hydrolysis, the untreated hydrolyzate was screened then flash-pasteurized. It was then cooled to 0° Centigrade and stored on board the ship. Peroxide was added to obtain a concentration of 0.5% by volume of oxygen. The hydrolyzate thus obtained was unloaded and shipped to the factory. It was reheated to 60° Centigrade, then transferred to the centrifuge, where the three fractions, J1, J2 and J3 were separated. The last two (J2 and J3) were then concentrated and spray-dried.

J1 – 58 kg

J2 – 113.40 kg

J3 – 94.40 kg

Water can be added on the basis of 50% of the weight of the fish, either at the time of the centrifuging or at the time of the hydrolysis (which was done in the example described here).

The analysis results are given below.

Analysis of a soluble product (fraction J3 in white powder) gave the following results, by way of example:

Ash = 8.7%; water content = 3.95%; Ether lipids = 0.6%; Chlorides (expressed as NaCl) = 2.6%; Phosphates as P<sub>2</sub>O<sub>5</sub> = 2.37%; Iron = 120 ppm; pH (water solution 1%) = 6; Aminated nitrogen (Sorensen) = 2.8%; Total nitrogen (N<sub>2</sub>) = 12.39%; Proteins (N<sub>2</sub> x 6.25) = 85.62%; aminated nitrogen = 0.205.

total nitrogen

By way of example, on an insoluble product (fraction J2 as a beige powder), the following results were obtained:

Ash = 5.06%; water content = 2.90%; Ether lipids = 13.60%; Chlorides (expressed as NaCl) = 0.65%; Phosphates as P<sub>2</sub>O<sub>5</sub> = 1.47%; Iron = 230 ppm; pH (water solution 1%) = 6.2; Aminated nitrogen (Sorensen) = 1.5%; Total nitrogen (N<sub>2</sub>) = 12.39%; Proteins (N<sub>2</sub> x 6.25) = 77.7%;

aminated nitrogen = 0.121.

total nitrogen

Still according to the example given above, the analysis results in grams of aminated acids per 100 grams of proteins are as follows:

Soluble product (fraction J3) as a white powder:

Lysine = 8.31; Histidine = 1.61; Arginine = 6.37; Aspartic acid = 9.45; Threonine = 4.06; Serine = 5.13; Glutamic acid = 15.57; Proline = 3.85; Glycocol = 8.80; Alanine = 6.75; Valine = 4.01; Methionine = 4.39; Isoleucine = 2.91; Leucine = 6.52; Tyrosine = 1.27; Phenylalanine = 1.71.  
Total = 90.71.

Insoluble product (fraction J2) as a beige powder:

Lysine = 6.07; Histidine = 1.61; Arginine = 3.94; Aspartic acid = 7.57; Threonine = 3.59; Serine = 3.87; Glutamic acid = 10.33; Proline = 2.9; Glycocol = 4.78; Alanine = 4.55; Valine = 3.53; Methionine = 4.33; Isoleucine = 2.97 Leucine = 6.02; Tyrosine = 1.96; Phenylalanine = 3.45.  
Total = 71.47.

The installation that permits production per the process is represented schematically in Figures 2, 3 and 4. It is divided into two parts: the first, through phase H inclusive, is installed on board ship. The second, starting with I, is on shore. The battery limit of the first part installed on board can be different from the one shown in the example.

A recovery tank 1 in the form of a hopper is located under the device for transferring and sorting freshly caught fish. This primarily involves non-marketable fish that are generally thrown back into the sea. An elevator 2 comprised, for example, of an endless screw, brings the fresh products over the grinder 3. The latter, of a conventional type, is equipped at 4 with finely perforated plates to produce a paste whose fragments are a few mm<sup>3</sup> in size.

The ground material is then picked up by a pump 5 and returned to the upper portion of two watertight tanks 6 and 7 used for the hydrolysis described above. Two valves (or cocks) 8 and 9 make it possible to fill these tanks in



alternating fashion. The hydrolysis is prepared and carried out in one of these tanks (light steam heating at 10 and 10a: possible addition of water at 11 and 11a) while the other tank is filling up. Additions of solution (or of aqueous solution) containing the exogenous enzymes at 12 or 12a are dosed and scheduled, in time, based on the cycle adopted for the hydrolysis. The role of the exogenous enzymes is defined in the text explaining the process. The medium is kept at a constant and controlled temperature on the order of about 56°, a temperature that is outside the zone where proteins are denatured and the endogenous enzymes are inactivated. The hydrolyzate is collected from each tank in alternating fashion through the piping 13. Valves 14 and 15 make it possible to stop the emptying of one or other of tanks 6 or 7. The movements of the cocks and valves can be automatically linked. The controls of apparatus such as pumps and the movements of valves constitute an automated and programmed whole. In this way, the hydrolysis time can be automatically set to a determined but variable value, by adjusting the heating time at 10 or 10a, and the solution transporting the exogenous enzymes at 12 and 12a. The purpose of these adjustments is to apportion in percentage terms the quantity of soluble products (fraction J3) to insoluble products (fraction J2). Solenoid valves installed at 10, 10a, 12 and 12a, equipped with timers or time switches, for example, complete the equipment. A programming unit also makes it possible to define the hydrolysis time for each category of product (in terms of the solubility of the products, for example).

Finally, a screening at 16 makes it possible to separate solid bodies such as bones, scales, etc., then recovering them through the manifold system equipped with a valve 17. The screen body includes a cleaning device. For example, a flow of seawater is created through the manifold 18 and exits through the same manifold 18a that is used for the pump's intake system 19. A three-way valve 20 enables both the normal course of the hydrolysates, when one of the tanks 6 or 7 is being emptied, and the evacuation of the wash waters (through 20a) after a tank full of the said hydrolyzate has been produced.

After the hydrolyzate has been sucked up through the screen 16, the pump 19 sends it into a watertight buffer tank 21. It is removed from this tank by the pump of a pasteurizer 22 (or, preferably, a flash pasteurizer), which works almost on a continuous basis thanks to the two tanks 6 or 7 and the buffer tank 21. According to the example given, the hydrolyzate is then sent through 23 to the holds of the ship where it is stored at 0° Centigrade, until return to port.

Peroxide in a low concentration of under 15 (or of a number of peroxides) may be added in the hydrolyzate circuit between 13 and 23. This proportional injection is done by a type of device mounted on the piping or on one of the volume spaces of this system.

After pumping and transportation in isothermal vessels, the hydrolyzate is sent by pump 24 into large-capacity tanks 25 and 26 installed in an on-shore plant. The product is then picked up by the same pump (24) and sent into a heating circuit that includes two volume spaces 27 and 28, an exchanger 29 and a system to permit stirring. A 30 and 30a, piping permits the addition of water.

A pump 31 picks up the hydrolyzate at a suitable temperature and sends it into a centrifuging separator 32. The lipid fraction J1 emerges from the latter and is collected in the flask 33 from which a new separation at 34 gives at 35 clear oils of very high quality. Also produced by the principal separator 32 are:

- The pasty fraction J2 (or paste), sent to the vessel 36.
- The aqueous solution J3 is sent to the flask 37, from which it goes into the clarifier 38. From the clarifier, the aqueous solution can be sent to the flask 39, then to the concentrator 40. It is stored in a concentrated state in the vessel 41. The residual paste coming out of the clarifier 38 is sent to the vessel 36. This vessel (fraction J2) and the vessel 41 (solution J3) separately feed the spray drier

42, through pumps 43 and 44. The products are then bagged or packaged or stored.

The concentrator 40 is of a type commonly used, for example a vacuum evaporator. As a variant, another concentrator can be placed between the vessel 36 and the pump 43 for fraction J2.

The circuit and the piping diagram proposed in the example cited are clearly not limiting. Therefore, the centrifuge and the concentrator can be doubled, tripled, etc. The connections among equipment items can be different in order to obtain all the combinations described above between operations L, M, N, Q and S (diagram in Figure 1).

When the complete installation is placed aboard the ship, the hydrolyzate goes directly from the pasteurizer 11 to temperature control and adjustment through pump 24 that pumps directly into the tank system and the heater (27, 28, 29). The test of the installation does not change.

It is self-evident, as can be seen from the foregoing, that the invention is not limited to the forms of embodiment described above. On the contrary, it covers all possible variants, provide they do not depart from the claims.

The application of this invention is the obtaining of food products or of food supplements to classic foods, which products or supplements must be right in fish proteins. This application covers both human and animal nutrition.

These manufacturing installations apply both to on-shore plants and to shipboard facilities.

Another application involves the manufacturing of therapeutic, dietetic or cosmetological products based on fish proteins or lipids, which can be used by both humans and animals.

Another application involves the obtaining of pure fish oils without solvents (using a mechanical process leading to Phase K).

## CLAIMS

1. Process for the enzymatic hydrolysis of fish proteins, said fish being processed immediately after being caught, said process involving the addition of exogenous enzymes, a process designed to produce hydrolyzates of different consistencies used for human nutrition without the addition of antibiotic-based preservative agents or of chelating agents, this process being characterized in that in the hydrolysis tank, the ground-up fish is in the form of a very fine powder with no added water, the time of hydrolysis of this ground fish and exogenous enzyme mixture being very short and capable of being adjusted in terms of the degree of solubility desired for the resulting foods.

2. The process of claim 1, characterized in that fresh water is added to the fish ground into a very fine paste mixed with exogenous enzymes, the duration of this hydrolysis being adjustable in terms of the quantity of soluble food products to be obtained.

3. The process of claim 1, characterized in that salt water is added to the fish ground into a very fine paste and the exogenous enzymes in the hydrolysis tank, the duration of this hydrolysis being adjustable in terms of the quantity of soluble food products to be obtained.

4. The process of claims 1, 2 and 3, characterized in that the hydrolysis in the tank takes approximately an average of one and a half hours.

5. The process of claims 1, 2 and 3 characterized in that the screening to separate out scales and bones takes place immediately upon emergence from the hydrolysis tank and prior to the flash-pasteurization.

6. The process of claims 1, 2 and 3, characterized in that the hydrolyzate is pasteurized (by flash-pasteurization) before being centrifuged for separation (possibly preceded by low temperature storage).

7. The process and resulting product of claim 6, characterized in that the lipid fraction (oil) is refined only by mechanical separation other than the separation (or separations) used to separate the untreated hydrolyzate after flash-pasteurization, which refining produces a clear oil obtained without solvent.

8. The process and resulting product of claim 6, characterized in that the pasty fraction (not very soluble) and the fraction consisting of the aqueous solution (soluble) can be treated together (concentration and drying), the solubility of the product obtained being in direct proportion to the duration of the hydrolysis (longer period of time).

9. The process and resulting product of claims 6 and 8, taken separately, characterized in that the concentration and drying installation located after the centrifuging includes three concentration and drying groups, one for each of the two fractions (pasty and aqueous), in order to treat them separately, and one group to treat them together.

10. The process of claims 1, 2 and 3, taken separately, characterized in that the hydrolyzate is stabilized by heating to around 90 to 100° so that the enzymes become permanently inactive, the hydrolyzate then being screened.

11. The process and resulting product of claims 1, 2, 3, 5 or 6, characterized in that the hydrolyzate is treated with one or more added peroxides, thereby reversibly inactivating the enzymes, the final product then becoming neutral in color.

12. The process and resulting product of claims 1 to 11, characterized in that the product is treated with a peroxide or similar substance in a less than 1% dilute solution, this peroxide having a deodorizing, decoloring and antiseptic action (but without causing the appearance of amino oxides) on any of the products obtained, the excess of such peroxide being destroyed during the separation phases or the drying phases.

13. The process and installation, of claims 1 to 12, taken separately, characterized in that the equipment necessary for the execution of the different phases, in addition to the normal means (tank for receiving the fish; conveyor; grinder; a starter jet pump to pump the ground fish; a hydrolysis tank with means for addition exogenous enzymes in solution or in suspension and for the injection of heating steam; screen; a starter jet pump; heaters and centrifuges; means for concentrating and heating), including at least one other hydrolysis tank, which hydrolysis tanks are either being filled or working, in alternating fashion, in order to obtain continuous and automatic treatment of the product, on which tanks the drains, the heating steam intakes, the addition of exogenous enzyme and any addition of water, are adjusted by timer-controlled valves that automatically adjust the hydrolysis time; this equipment also includes at least one flash-pasteurizer.

14. The process and installation of claims 1, 6 and 13, taken together, characterized in that all the phases of the process are carried out on board ship, including the separation and drying of the products.

15. The process and installation of claims 1, 6 and 13, taken together, characterized by the fact that all the phases of the product are carried out in an onshore plant.

[Three pages of illustrations follow]



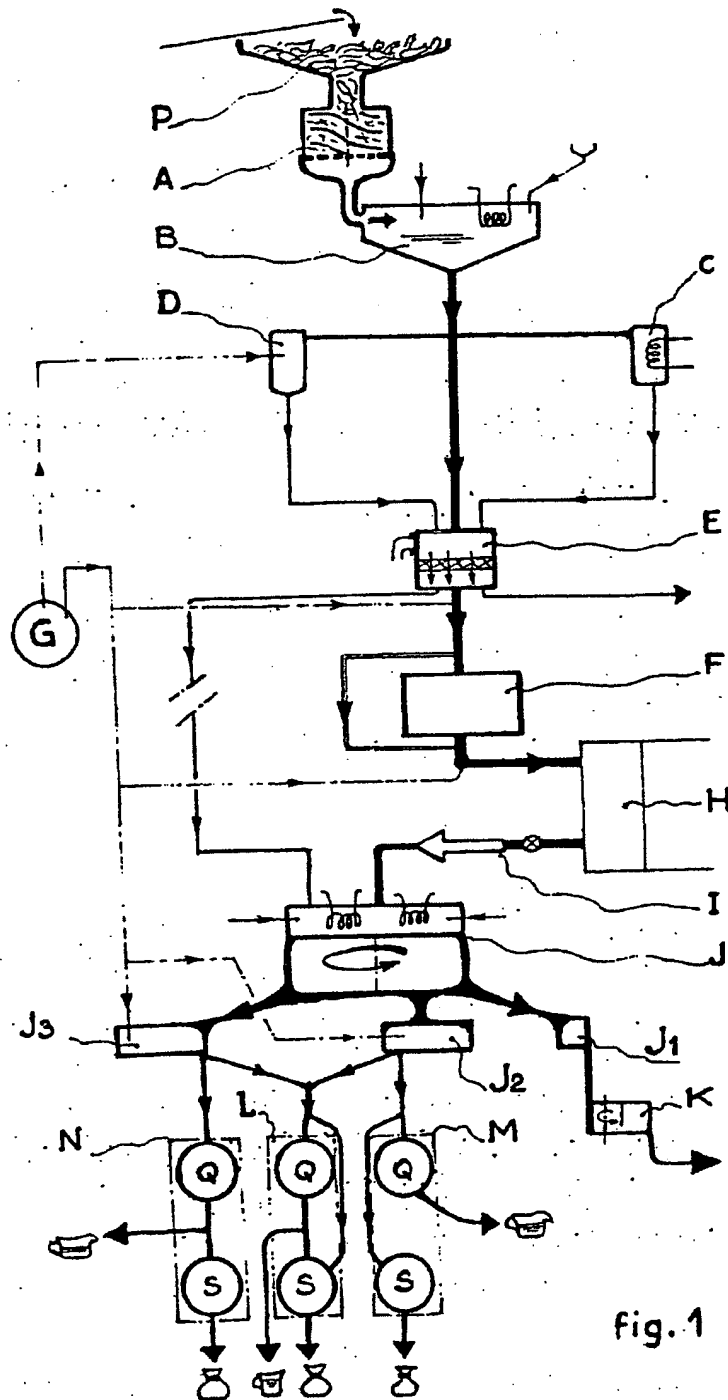


fig. 1

PL. II-3

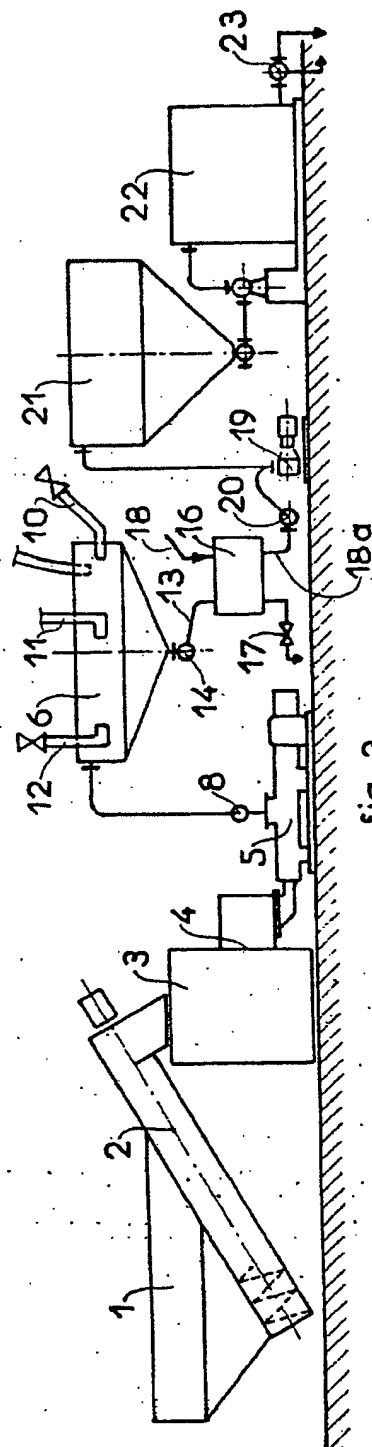


fig. 2

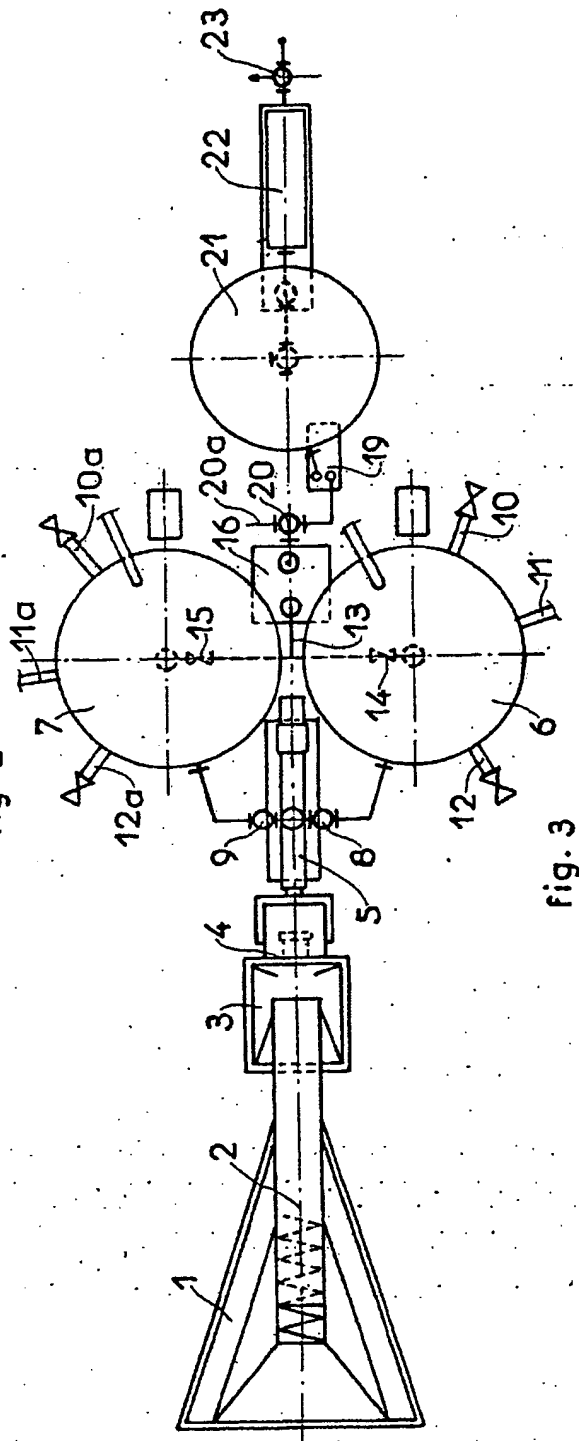


fig. 3

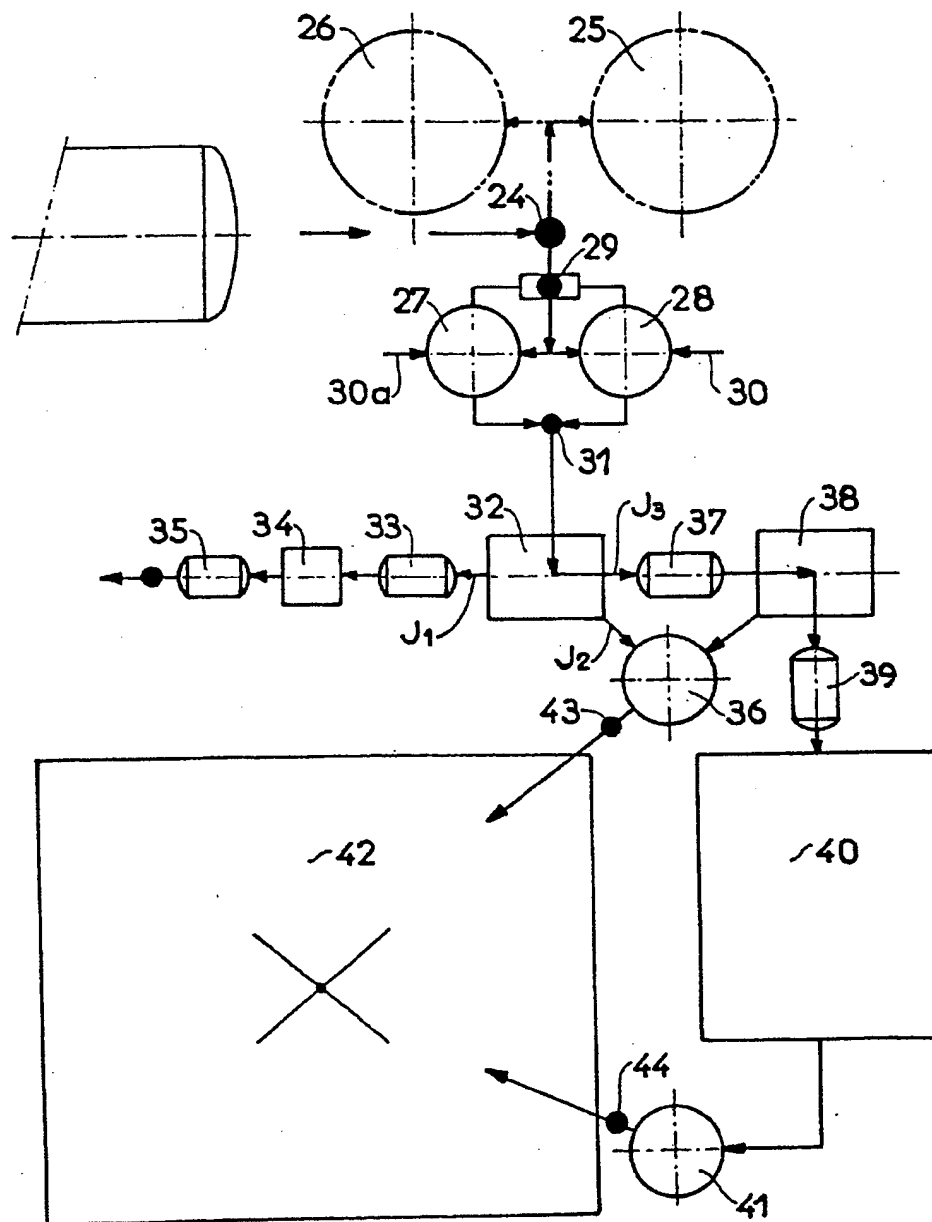


fig. 4